

Photometric Determination of Tin in Iron and Steel. III : Photometric Determination of Tin with Sodium Diethyldithiocarbamate

| | |
|------------------------------|--|
| 著者 | GOTO Hidehiro, KAKITA Yachiyo |
| journal or publication title | Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy |
| volume | 9 |
| page range | 253-261 |
| year | 1957 |
| URL | http://hdl.handle.net/10097/26829 |

Photometric Determination of Tin in Iron and Steel. III

Photometric Determination of Tin with Sodium Diethyldithiocarbamate*

Hidehiro GOTÔ and Yachiyo KAKITA

The Research Institute for Iron, Steel and Other Metals

(Received May 2, 1957)

Synopsis

In continuation of the work reported previously, photometric determination of micro-quantities of tin in iron and steel was investigated by using sodium diethyldithiocarbamate. Tin was separated from a large amount of iron by coprecipitation with manganese dioxide as reported previously, and then the photometric determination was made after extracting tin as its diethyldithiocarbamate complex with an organic solvent. Using 1 g of sample, the determination of 0.001 per cent content of tin was possible by this method.

I. Introduction

In the previous paper of this series,⁽¹⁾ photometric determination of micro-quantities of tin in iron and steel by the reaction between tin (II) and cacotheline was reported. Later, studies were made on the same determination by using sodium diethyldithiocarbamate. Numerous works have been made⁽²⁾ on the photometric determination of various metals by using sodium diethyldithiocarbamate, but none of them referred to the determination of tin in iron and steel. Therefore, this point was examined in the present work. Separation of tin from iron was made by coprecipitation with manganese dioxide, as in the previous case.

II. Photometric determination of tin

1. Apparatus and reagents

(i) Apparatus

The Pulfrich's photometer was chiefly used. The light source was an incandescent lamp and 1 cm cell was used. Absorption curve was obtained by Beckman Model DU spectrophotometer. Extraction was carried out with about 200 ml separating funnel.

(ii) Reagents

Standard tin solution: 0.2500 g of tin metal (analytical pure grade, Merck)

* The 881st report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute for Metals, **20** (1956), 319.

(1) H. Gotô and Y. Kakita, J. Japan Inst. Metals, **17** (1953), 220, 223; R. I. T. U. A. **6** (1954), 1, 12.

(2) J. Davis, A. J. Easton, Metal Ind., **82** (1953), 418; Yu. A. Chernikhav, B. M. Dobkina, Zavodskaya Lab., **15** (1949); Chem. Abst., **44** (1950), 1358; Rene J. Lacaste, Mason H. Earing, Stephen E. Wiberly, Anal. Chem., **23** (1951), 871; E. Sudo, J. Chem., Soc. Japan, **73** (1952), 626; 693; 753; Helmut Bode, Z. anal. Chem., **143** (1954), 182.

was dissolved in a mixture of 30 ml of hydrochloric acid (1 + 1) and 10 ml of nitric acid (1 + 1) by heating and then cooled. The whole volume brought to 500 ml with hydrochloric acid (1 + 1). This solution contains 0.5 mg of tin per ml.

Sodium diethyldithiocarbamate solution: 0.5 per cent aqueous solution.

Organic solvents: Benzene, chloroform, carbon tetrachloride, xylene, amyl alcohol, amyl acetate and petroleum ether used were the analytical pure grade.

2. Experimental method

A definite amount of the tin solution was placed in the separating funnel, hydrochloric acid and sodium diethyldithiocarbamate solution were added, and the mixture was shaken vigorously with an organic solvent for a definite time. The organic solvent layer was then separated and its optical density was measured.

3. Selection of organic solvent

Tin and diethyldithiocarbamate produces a white precipitate in weak acid solution but when the concentration of tin is low, the solution seems colorless and clear. This solution can be extracted with an organic solvent, such as chloroform or benzene, and the organic solvent layer becomes yellow. The extraction can be effected with benzene, chloroform, carbon tetrachloride, xylene, amyl alcohol and amyl acetate, the extracted solution coloring yellow. The extraction is not effected with petroleum ether. Of the foregoing organic solvents benzene and chloroform showed good extractibility but benzene was used in the present experiments because of its low cost.

4. Absorption curve

A mixture of 25 or 50 γ of tin, 5 ml of sodium diethyldithiocarbamate solution

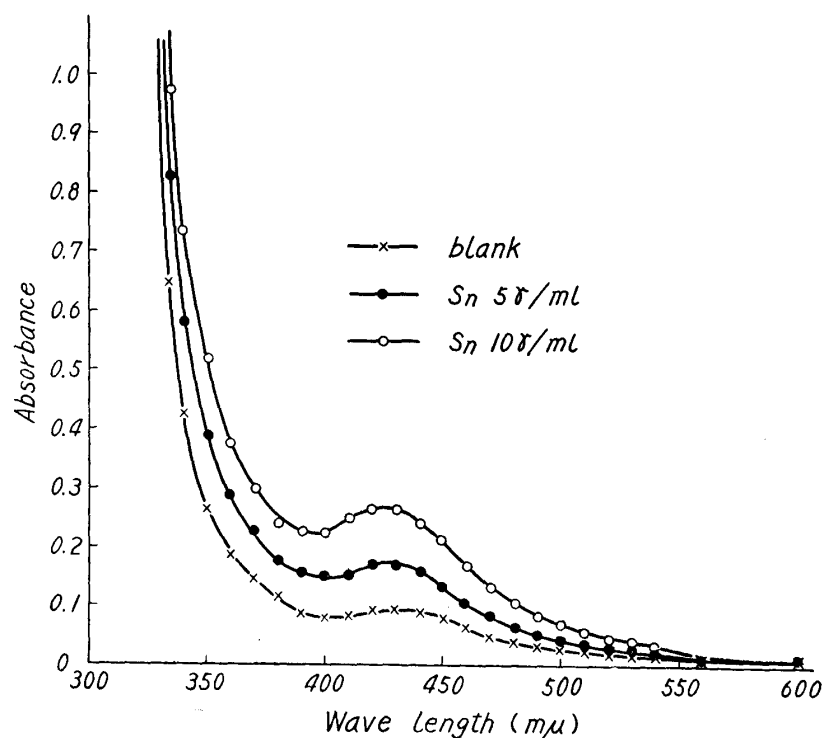


Fig. 1. Absorption curve, vs. benzen.

and a certain quantity of 0.05N hydrochloric acid to bring the total volume to 60 ml, was extracted with 5 ml of benzene. Transmittance of the benzene extract at 320~700 $m\mu$ was measured with the Beckman Model DU spectrophotometer and absorption curve was obtained.

Fig. 1 shows the result of measurement with benzene as the standard. The blank test also exhibited a strong absorption in the ultraviolet region and both showed similar curves. In order to obtain better absorption due to coloration of tin alone, absorption was measured with the extract of blank test as the standard. Results of this measurement are shown in Fig. 2. There is a maximum absorption at 330 $m\mu$, the molecular absorption coefficient at this point being 6354. When the measurement is made with the Pulfrich's photometer, it is better to use the absorption at 434 $m\mu$, the molecular absorption coefficient being 2262.

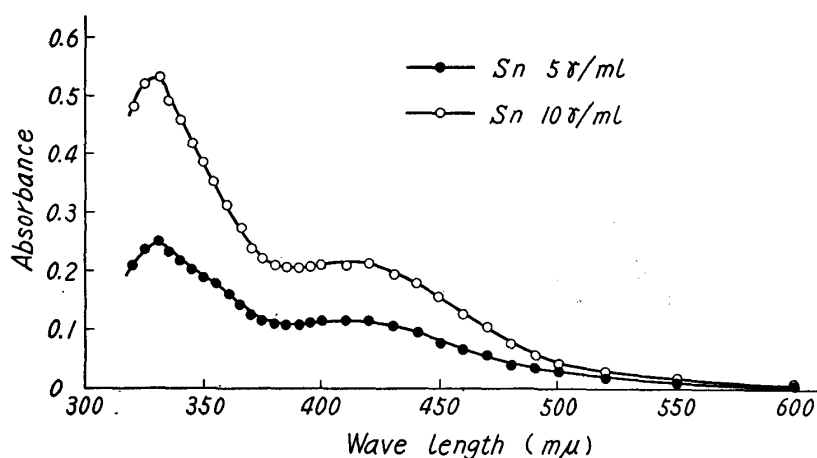


Fig. 2. Absorption curve, vs. blank solution.

5. Concentration of hydrochloric acid

Davis and others⁽²⁾ reported that the extraction was complete at pH 5.8~6.0 and that the values observed were lower under other conditions. A mixture of 0.25 mg of tin and 5 ml of sodium diethyldiethiocarbamate was brought to a total volume of 60 ml with various concentrations of hydrochloric acid and extracted with 5 ml of benzene. Optical density of this benzene extract was measured with benzene as the standard, by using the Pulfrich's photometer, with S_{43} (434 $m\mu$) filter. Results obtained are shown in Table 1. The range in which the pH

Table 1. Concentration of hydrochloric acid.

| pH | HCl (N) | Absorbance measured | |
|-----|---------|---------------------|-------|
| 7.6 | | 0.060 | 0.061 |
| 5.6 | | 0.252 | 0.250 |
| 4.0 | | 0.330 | 0.332 |
| 3.0 | | 0.345 | 0.347 |
| 2.2 | | 0.360 | 0.360 |
| 1.2 | | 0.360 | 0.361 |
| | 0.10 | 0.363 | 0.360 |
| | 0.15 | 0.363 | 0.361 |
| | 0.20 | 0.350 | 0.353 |
| | 0.30 | 0.280 | 0.281 |
| | 0.40 | 0.230 | 0.228 |

measurement is facile is indicated by pH and that in which such is difficult is indicated by the concentration (N) of hydrochloric acid.

As shown in Table 1, a definite absorption is obtained in the range of pH 2.2 to 0.15N of hydrochloric acid concentration. It was also shown that the separation of benzene and water layers was much more rapid as the concentration of the acid increases.

6. Amount of sodium diethyldithiocarbamate

Using 0.05N hydrochloric acid and various amounts of sodium diethyldithiocarbamate, the mixture was extracted with 5 ml of benzene and the optical density of such benzene extracts was measured with the S_{43} filter. Results are shown in Table 2.

Table 2. Amount of sodium diethyldithiocarbamate (DDC).

| DDC (0.5%) added (ml) | Absorbance measured | | Absorbance |
|-----------------------------|---------------------|-------|------------|
| | Sn 0.25 mg | Blank | |
| 1 | 0.248 | 0.015 | 0.233 |
| | 0.250 | 0.016 | 0.234 |
| 2 | 0.328 | 0.016 | 0.312 |
| | 0.328 | 0.014 | 0.314 |
| 3 | 0.360 | 0.018 | 0.342 |
| | 0.359 | 0.014 | 0.345 |
| 4 | 0.362 | 0.018 | 0.344 |
| | 0.360 | 0.017 | 0.343 |
| 5 | 0.362 | 0.019 | 0.343 |
| | 0.363 | 0.020 | 0.343 |
| 6 | 0.365 | 0.023 | 0.342 |
| | 0.366 | 0.024 | 0.342 |
| 7 | 0.372 | 0.029 | 0.343 |
| | 0.370 | 0.026 | 0.344 |

As shown in Table 2, a constant absorbance is obtained by using 0.5 per cent sodium diethyldithiocarbamate above 3 ml. A larger amount of sodium diethyldithiocarbamate results in some increase in blank value.

7. Relationship between the amount of tin and absorbance

Various amounts of tin with 5 ml of sodium diethyldithiocarbamate solution were brought to a total volume of 60 ml with 0.05N hydrochloric acid and extracted with 5 ml of benzene, and optical density of the extracts was measured with the Pulfrich's photometer with S_{43} filter by using benzene as the standard. Results are shown in Fig. 3, I.

As shown by the curve I in Fig. 3, the amount of tin and absorbance are in linear relationship.

8. Effects of other ions

When precipitates formed from various metals with sodium diethyldithio-

carbamate are extracted with an organic solvent, they show various colorations, and so such solutions are usually used for photometric determinations.⁽²⁾ Conditions under which these metal complexes were extracted and the wave length at which maximum absorptions occur were different with different metals, but it is certain that they greatly affect the determination of tin. As many of these points have been examined in detail, none was made in the present experiment. With a few of such metals that directly interfere in the determination of tin, the method of removing such an effect was examined. As reported in the preceding paper,⁽¹⁾

the separation of tin from iron was made by coprecipitation with manganese dioxide and antimony and arsenic were also coprecipitated with manganese dioxide. However, a trace of iron always accompanied tin even by two procedures with manganese dioxide. Therefore, samples of tin separated from iron by such a method was always contaminated with a large amount of manganese and a small amount of antimony, arsenic and iron.

(i) Removal of manganese effect

Determination of tin with sodium diethyldithiocarbamate was made in weak hydrochloric acidity, but the reaction of manganese and the carbamate was more sensitive in the neutral or slightly alkaline range and very weak in acid range. However, the amount of manganese was usually so larger than that of tin that its effect was fairly great. After various examinations, it was found that sodium diethyldithiocarbamate was extracted well with petroleum ether. The diethyl dithiocarbamate complex of manganese was weakly combined in weakly acidic solution and the complex under went decomposition when the mixture was shaken with petroleum ether, the diethyl dithiocarbamic acid being extracted with petroleum ether and manganese remaining in the acid layer. The diethyldithiocarbamate complex of tin was strongly combined in weak acid solution and remained in the acid solution on being shaken with petroleum ether, being neither decomposed nor extracted.

(a) Removal of manganese effect with petroleum ether

A mixture of tin and manganese with 5 ml of sodium diethyldithiocarbamate was brought to a total volume of 60 ml with 0.05N hydrochloric acid, and shaken with 10 ml of petroleum ether for about 1 minute. Aqueous layer was separated and shaken with 5 ml of benzene. Optical density of the benzene extract was measured, and the results are shown in Table 3.

As shown in Table 3, the values obtained are higher due to the effect of manganese when extraction with petroleum ether is not carried out. The

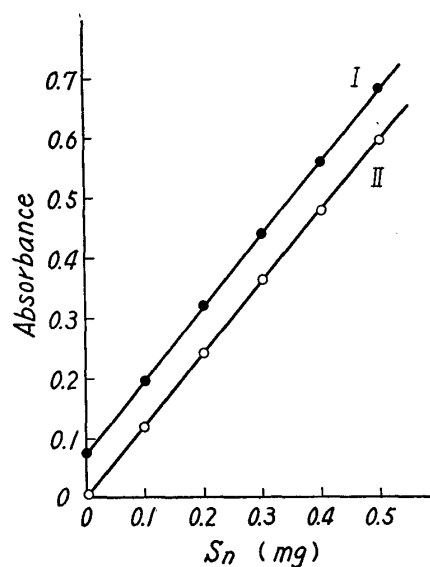


Fig. 3. Calibration curves.

petroleum ether extraction seems to have no effect on tin.

Table 3. Removal of influence of Manganese.

| Sn taken (mg) | Mn added (mg) | Absorbance measured | Absorbance |
|------------------|------------------|------------------------|----------------|
| *0 0 | 0 0 | 0.074 0.050 | — — |
| *0 0 | 80 80 | 0.180 0.051 | 0.106 0.001 |
| *0.25 0.25 | 80 80 | 0.485 0.365 | 0.411 0.315 |
| *0.25 0.25 | 0 0 | 0.387 0.362 | 0.313 0.312 |

* Not extracted with petroleum ether.

The same test was made with samples containing a large amount of manganese. The amount of petroleum ether used for the first extraction was 10 ml and that for the second extraction was 5 ml. Up to 130 mg of manganese, twice extractions with such amount were sufficient but with 160 mg or so of manganese, twice extractions were not good enough and further extraction was necessary. There was no effect on tin with such twice extractions with petroleum ether, and the blank value could be brought almost to zero by this method.

(b) Relationship between tin and absorbance after removal of manganese effect with petroleum ether extraction

The foregoing experiments showed that the effect of manganese could be removed by extraction with petroleum ether without affecting the determination of tin. Therefore, various amounts of tin were used in a mixture with 80 mg of manganese and 5 ml of sodium diethyldithiocarbamate solution, the total volume brought to 60 ml with 0.05N hydrochloric acid was extracted twice with 10 and 5 ml of petroleum ether, the aqueous solution separated was extracted with 5 ml of benzene and optical density of the benzene extract was measured. Result obtained is shown by curve II in Fig. 3, which shows linear relationship between the amount of tin and absorbance, parallel to curve I. This result also shows no effect of petroleum ether extraction on the determination of tin.

(ii) Effect of arsenic and antimony

Addition of sodium diethyldithiocarbamate to a solution containing antimony produced a white turbidity which was incompletely extracted with benzene, and the extract remained almost colorless, although a slightly yellow coloration occurred when the amount of antimony was large. The trace of antimony present in iron and steel is almost negligible when it is determined with S_{43} filter, and so its removal was not undertaken.

Arsenic (III) complex was similarly extracted with benzene, whose extract remained colorless, but the extracted solution showed a strong absorption in the ultraviolet region according to Sudô.⁽²⁾ However, the absorption of arsenic complex

was not observed when $S_{43}(434\text{ m}\mu)$ filter was used, and so the effect of antimony might be disregarded.

(iii) Removal of iron

Iron produced a dark brown precipitate with sodium diethyldithiocarbamate and the precipitate was extracted with benzene, which colored dark brown. This coloration was extremely sensitive. When the amount of iron was small this precipitate became colloidal and could not be filtered but the precipitate coagulated on shaking the mixture with petroleum ether, collecting as a precipitate between the two solvent layers. This could easily be separated by filtration.

9. Effect of valency of tin

The foregoing experiments were carried out on quadrivalent tin and further experiments were carried out on bivalent tin for the sake of comparison. Reduction was carried out with aluminium foil used as a cigaret wrapper. To a mixture of 0.25 mg of tin in 1 ml of 3N hydrochloric acid and about 5 ml of water, 0.16 g of aluminium was added and heated in carbon dioxide atmosphere to reduce Sn^{4+} to Sn^{2+} . After complete dissolution of aluminium, the mixture was cooled, and the whole volume was brought to about 60 ml with freshly boiled and air-free cooled water. On the other hand, aluminium alone was dissolved in hydrochloric acid, the total volume was made up similarly to 60 ml and 0.25 mg of Sn^{4+} was added. Each of such solutions was mixed with 5 ml of sodium diethyldithiocarbamate solution, shaken vigorously for about 1 minute with about 10 ml of petroleum ether, after standing the ether layer was separated and the aqueous layer was filtered through a filter paper. The filtrate was extracted with 5 ml of benzene and the absorbance of the benzene extract was measured. It was found that the extracted solution of bivalent tin obtained by reduction with aluminium showed absorbance of 0.314 and 0.315, whereas that obtained from the addition of quadrivalent tin to a solution of aluminium showed absorbance of 0.315 and 0.313, and the solution obtained from extraction of quadrivalent tin itself showed 0.315 and 0.313. Thus, both bivalent and quadrivalent tin showed the same color tone and absorbance.

III. Photometric determination of tin in iron and steel

Based on the foregoing experimental results, an analytical procedure for the determination of tin in iron and steel samples described below was proposed, by using the same method of coprecipitation with manganese dioxide as reported earlier⁽¹⁾ for separating tin from iron.

1. Analytical procedure

A solution of 0.2~1.0 g of the sample dissolved in 20 ml of nitric acid (1+1) with heating is added with about 80 ml of water and 5 ml of 5 per cent manganese nitrate solution and the mixture is boiled while adding 3 ml of 1N potassium permanganate solution in small portions. The mixture is boiled further to precipitate manganese dioxide and allowed to stand for about 10 minutes. This is filtered through a filter paper, the precipitate is washed with warm water, and the

majority of the precipitate is transferred to the original beaker. The precipitate remaining on the filter is dissolved by pouring 10 ml of nitric acid (1+1) and a small amount of hydrogen peroxide, and the filtrate is received in the beaker containing majority of the precipitate. The filter is washed with hot water and the combined filtrate and washings is boiled to dissolve the precipitate and decomposed hydrogen peroxide. The volume is brought to about 100 ml with addition of water, similarly treated with 1N potassium permanganate solution, and the precipitate is collected by filtration. After washing with hot water, a majority of the precipitate is transferred to the original beaker. The precipitate remaining on the filter is dissolved by pouring over it a mixture of 1 ml of 3N hydrochloric acid, a few drops of 30 per cent hydrogen peroxide and about 15 ml of water. The filtrate is received in the beaker containing the precipitate, the filter is washed with warm water, and the combined filtrate and washing is boiled to decompose hydrogen peroxide. After cooled, the solution is transferred to a 200 ml separating funnel and the total volume is brought to about 60 ml. 5 ml of sodium diethyldithiocarbamate solution is added to this solution, shaken vigorously for about 1 minute with 10 ml of petroleum ether and the ether layer is separated after standing. The aqueous layer is again shaken with 5 ml of petroleum ether similarly, and the aqueous layer separated is rapidly filtered through a small filter paper. The solution is passed perfectly and the filter is not washed. The filtrate is transferred to a well-washed separating funnel, about 5 ml of benzene is added through a burette and the mixture is shaken vigorously for about 1 minute. The benzene layer is separated, transferred to the 1 cm cell of the Pulfrich's photometer and its absorbance is measured by using incandescent lamp as the light source, using $S_{43}(434\text{ m}\mu)$ filter and benzene as the standard. The amount of tin

Table 4. Results obtained on the determination of tin.

| Sample | Sample taken (g) | Absorbance | Sn obtained (mg) | Sn (%) | Sn mean (%) | Cacoteline method (%) | Volumetric method (%) |
|------------|------------------|------------|------------------|--------|-------------|-----------------------|-----------------------|
| Steel 1 | 0.5000 | 0.240 | 0.195 | 0.039 | 0.039 | 0.038 | 0.031 |
| | 0.5000 | 0.235 | 0.190 | 0.038 | | | |
| Steel 2 | 0.5000 | 0.245 | 0.200 | 0.040 | 0.040 | 0.040 | 0.032 |
| | 0.5000 | 0.247 | 0.202 | 0.040 | | | |
| Steel 3 | 1.0000 | 0.318 | 0.260 | 0.026 | 0.026 | 0.025 | — |
| | 1.0000 | 0.313 | 0.258 | 0.026 | | | |
| Steel 4 | 0.5000 | 0.375 | 0.310 | 0.062 | 0.063 | 0.064 | — |
| | 0.5000 | 0.378 | 0.313 | 0.063 | | | |
| Steel 5 | 0.5000 | 0.275 | 0.225 | 0.045 | 0.045 | 0.045 | — |
| | 0.5000 | 0.270 | 0.220 | 0.044 | | | |
| Soft-steel | 0.5000 | 0.293 | 0.240 | 0.048 | 0.048 | 0.049 | — |
| | 0.5000 | 0.295 | 0.242 | 0.048 | | | |
| C-steel | 0.5000 | 0.070 | 0.050 | 0.005 | 0.006 | 0.005 | — |
| | 0.5000 | 0.075 | 0.055 | 0.006 | | | |

is calculated from the absorbance obtained and the calibration curve. The use of spectrophotometer at the wave length $330\text{ m}\mu$, at which the maximum absorption appears, will give better sensitivity, but in some samples, the effect of arsenic and antimony must also be considered with such wave length.

2. Analytical results

Results obtained on the determination of tin in various samples of iron and steel by the foregoing procedures are shown in Table 4. As shown in Table 4, analytical results by the present method coincide well with those obtained by the cacotheline method.⁽¹⁾

Summary

- (1) Photometric determination of tin was carried out by extraction of a complex salt of tin and sodium diethyldithiocarbamate with an organic solvent by using chiefly the Pulfrich's photometer.
- (2) Of the various organic solvents examined, chloroform and benzene showed excellent results, but benzene was used in the present series of experiments.
- (3) Absorption curve was obtained by the use of the Beckman spectrophotometer and a maximum absorption appeared at $330\text{ m}\mu$.
- (4) The suitable concentration of the acid for complete extraction was found to be from pH 2.2 to 0.15N of hydrochloric acid concentration.
- (5) Separation of tin from iron was effected by coprecipitation of tin with manganese dioxide, and interfering effect of manganese and a trace of iron occluded could be removed by extraction with petroleum ether.
- (6) Based on the foregoing experiments, an analytical procedure for the determination of microquantities of tin in iron and steel was proposed.